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A Top Surface Imaging Method Using Area Selective ALD on Chemically Amplified Polymer Photoresist Films

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A method for performing top surface imaging (TSI) on a single polymeric photoresist film using area selective atomic layer deposition (ALD) is presented. In this method, exposure of the polymer thin film creates reactive hydroxyl sites on the film surface in the exposed areas that subsequently act as nucleation and growth sites for deposition of metal oxide features using a chemically selective atomic layer deposition process. Specifically, it is shown that titanium isopropoxide and water can be used as ALD precursors in conjunction with a chemically amplified photoresist film, formulated using a protected polymer [poly(*tert*-butyl methacrylate)] and a photoacid generator [triphenylsulfonium tris(perfluoromethanesulfonyl)methide], to successfully perform such an area selective ALD TSI process. Using this material set and methodology, micrometer-scale photoresist features are defined, metal oxide patterns are produced, and these patterns have been transferred through the polymer film via plasma etching. One unique feature of this TSI process is that it has been achieved without requiring a descum etch, which is commonly needed with other TSI methods, due to the highly selective nature of the ALD process.
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The continued quest for miniaturization of feature sizes in microelectronic, optoelectronic, and microelectromechanical systems places strong demands on the lithographic and patterning processes used to fabricate such devices. In particular, semiconductor device manufacturing is continuing to push the limits of the high-volume optical lithography processes and materials used for fabricating device features beyond the 45 nm technology node. Developing so-called single layer resist (SLR) materials and processes that can enable such high-resolution patterning methods in the face of the extremely limited focus latitude available in modern optical projection lithography tools and yet still provide sufficient etch barrier toughness continues to be a significant challenge and potential future roadblock. In SLR approaches, these two issues are coupled because they both depend directly on the resist film thickness. One way to overcome these issues is to decouple the depth of focus limitation from the etch barrier toughness by transitioning to bilayer resist materials and processes. The basic idea in these bilayer methods is to form the initial pattern in an extremely thin imaging film, which is coated onto a thicker etch barrier layer, and subsequently transfer that pattern through the etch barrier layer via etching techniques to form the final resist pattern. Such bilayer methods have been developed but have suffered from a number of problems including material compatibility limitations which inhibit materials design flexibility, process complexity of the multiple coating steps required, and difficulty in controlling deposition of the extremely thin imaging film layers.[1-3] A related but different approach is to employ so-called top surface imaging approaches, in which a single layer resist is subsequently chemically modified in its surface or near-surface region after patternwise exposure to render selected regions of the resist film surface more resistant to subsequent etching processes.[1,4-7] Again, the final patterned resist is formed by transferring the pattern formed by exposure and chemical modification of the resist surface throughout the entire resist film thickness by an etching technique.

Such top surface imaging (TSI) techniques using vapor or liquid phase silylation have been investigated extensively as alternatives to conventional resist processing. A variety of different process schemes including Si-CARL, DESIRE,[5] PRIME,[7] SUPER,[6] and digital-top-surface-imaging,[4] have been considered over the past 20 years. Ideally, TSI via silylation methods involves the selective silylation of specific regions of a resist while the other regions are not silylated, i.e., the incorporation of silicon into either only the exposed or unexposed regions of the resist film. Patterns are obtained by selectively etching away the unsilylated regions with an oxygen plasma. In these cases, the silicon present in silylated regions forms a glassy SiO_2 layer on the resist surface during the early stages of the oxygen plasma etch, which serves as an oxygen plasma etch barrier and prevents further etching of the underlying organic resist layer in the silylated regions.[3-5,8]

TSI imaging schemes have several potential benefits. Because only the top portion of the resist film is imaged, the resist may be relatively opaque at the wavelength of the imaging tool, thus allowing the use of a wider variety of organic resist materials with a particular exposure wavelength. In addition, because the imaging reaction in principle only needs to occur in the surface layer of the resist film, the required depth of focus for the imaging tool and process can be minimized and the resist film thickness can be arbitrarily large, thereby widening the process window of the imaging and etch processes. A further advantage is that extremely high aspect ratio resist features can be produced because the development of the pattern in the organic film is achieved by pattern transfer from the surface image into the bulk of the organic resist film, using a plasma etch which can be tailored to be highly anisotropic. One final advantage is that resist pattern collapse that is encountered in the wet development of conventional SLR materials can be avoided in TSI processes because a wet development step of the resist features is never required. However, a variety of difficulties has limited the successful application of such TSI approaches. One of the main challenges with TSI processes has been finding ways to reduce the line edge roughness (LER) of the TSI-generated patterns to within acceptable values (i.e., the ITRS roadmap shows requirements for LER $3\sigma < 6$ nm at the 65 nm node and 4.2 nm at the 45 nm node).[3,4,9-11] Earlier imaging schemes such as DESIRE relied on cross-linking of the polymer resist film in the exposed areas to slow the diffusion of the silylating agent into the exposed areas, thus producing different concentrations of Si in the exposed and unexposed regions. Because some Si remained, even in exposed regions where it was not desired, a plasma descum process was required to remove the thin layer of silicon incorporated into the cross-linked regions before performing the O_2 plasma pattern transfer etch.[4,5] Furthermore, differences in the cross-linking density and subsequent amount of silicon incorporation across the width of an optically projection printed feature led to nonuniform silylation profiles, commonly referred to as bird's beak profiles, which ultimately led to difficulty with critical dimension (CD) control of the feature and increased the LER of the overall process. So-called digital silylation techniques were developed to overcome these problems with the cross-linking-based silylation processes. Digital silylation offered the potential to eliminate the need for a descum step because the

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active sites on the polymer which participate in the silylation are generated during exposure and postexposure baking (PEB) of the resist. In this manner, the unexposed areas are nominally unreactive toward the silylating agents and thus a descum etch is in principle not required.[4] However, due to the nonuniform energy deposition profile across a feature which results from the nonideal aerial image produced using optical projection tools, the concentration of active sites in the exposed polymer varies across the feature width. The amount of Si incorporated into the near-surface volume of such features using the digital silylation processes thus decreases from the feature center to the feature edges. Therefore, the thickness of the silicon etch barrier formed at the feature edges is still thinner than the bulk of the feature, and so it does not serve as an effective etch mask in the oxygen plasma, which still results in CD control problems and unacceptable LER. One solution to help reduce such CD control and LER problems in digital silylation processes is to perform a trim or descum etch to remove the very thin silylated regions of the features at the feature edges, but such issues are still a major problem.

Recently, significant efforts have been undertaken to develop area selective atomic layer deposition techniques (ASALDT).[12-15] During atomic layer deposition (ALD), thin-film growth is controlled by self-limiting surface reactions. Thus, if a surface can be modified to prevent the surface reactions involved in the ALD process, nucleation and film growth during ALD can also be prevented on those regions of the surface. ASALDT utilizes this approach to block nucleation in certain areas while allowing film deposition only in desired areas. Early studies focused on the use of self-assembled monolayers (SAM) as masks for achieving area selective ALD of metal oxides on Si substrates and reported the use of octadecyltrichlorosilane SAMs to inhibit nucleation of ALD films.[12,13] More recently, the authors have shown that patterned polymer films can provide a much more robust and simpler method for achieving selective ALD.[14,15] In these previous studies, micrometer-scale direct patterned deposition of TiO_2 on Si was achieved using titanium tetrachloride or titanium isopropoxide as the metal precursor, water as an oxygen source, and poly(methyl methacrylate) as a photodefinable polymeric masking layer. These recent investigations have demonstrated that nucleation of titania films produced by ALD can be successfully blocked on polymer materials that do not contain reactive OH groups in their backbone. In addition, it was observed that under surface conditions where ALD films do nucleate on the polymer film, a conformal and defect-free film can be formed directly on the polymer surface. These earlier studies ultimately inspired the TSI technique presented here.

In this paper, a method for utilizing area selective ALD to perform TSI is presented. The approach involves the selective deposition of an inorganic etch barrier, i.e., a metal oxide in this work, on predefined reactive areas of a polymer film surface which have been delineated by radiation exposure, followed by selective etching of the regions of the polymer film not masked by the etch barrier layer to obtain the desired resist pattern. Figure 1 illustrates the process scheme utilized in this TSI process. This TSI method offers the potential to overcome the problem of thin etch barrier thickness at the feature edge encountered in other TSI methods which results from low silicon incorporation at the feature edge. In the ALD-based TSI approach presented here, the amount of etch barrier material incorporated into the film structure does not depend on the total concentration of active sites generated in the exposed polymer volume as is the case with previous TSI approaches. The nucleation of the ALD film growth in the method presented here depends only on the presence of active sites on the polymer film surface. Thus, the thickness and amount of ALD etch barrier deposited does not depend on the total hydroxyl concentration in the volume of the polymer film but instead depends on the number of ALD growth cycles performed. Therefore, it should be possible to use ALD to grow thicker, more robust etch barrier layers that can withstand the plasma pattern transfer etching processes and thus help to reduce LER in such features. Finally, because deposition of the etch barrier material can be extremely selective, a plasma descum etch is not required, which offers the potential to simplify the overall imaging process. While there are many questions that must be answered to fully validate the promise of such a technique, this paper reports preliminary experimental results that demonstrate the feasibility of achieving TSI using an area selective ALD process on polymer films.

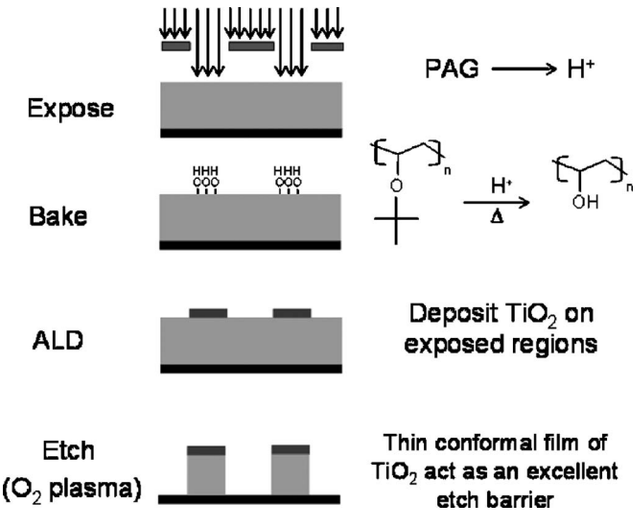

Figure 1. Schematic of the top surface imaging approach which utilizes area selective atomic layer deposition in conjunction with a radiation sensitive reactive polymer film to achieve direct patterned deposition of an etch barrier film.

Experimental

Poly(*tert*-butyl methacrylate) (PtBMA) (Scientific Polymer) was used as a model resist film for the area selective ALD TSI process because it does not contain OH groups and the *tert*-butyl ester group can undergo acid catalyzed de-esterification to produce hydroxyl containing polymethacrylic acid (PMAA).[16] A 5 wt % solution of PtBMA in toluene was mixed with 1 wt % (by solids) triphenylsulfonium tris(perfluoromethanesulfonyl)methide (3M Corporation), which serves as a photoacid generator (PAG). Resist films were spin coated onto a Si⟨100⟩ wafer and then soft baked at 90°C for 4 min to remove residual casting solvent. Ultraviolet (UV) exposure of the resulting films was performed at a total dose of 60 mJ/cm^2 using an Oriel 87000 series DUV exposure tool. The exposure tool was equipped with 500 W Hg-Xe lamp and an external bandpass filter (center wavelength of 248 nm and full width at half-maximum of approximately 20 nm) that narrowed the spectral width of the UV radiation. All exposures were conducted in a base-free cleanroom environment and a postexposure bake (PEB) was conducted immediately after exposure at 130°C for 15–20 s to promote the acid catalyzed deprotection reaction of the polymer. After PEB, films were exposed to room ambient where airborne base quickly quenched excess acid present in the exposed regions of the film. Acid generated in the exposed regions of the film resulted in cleavage of the *tert*-butyl ester groups on the polymer to produce PMAA in the presence of moisture after baking. Figure 2 shows Fourier transform infrared (FTIR) spectra of the starting PtBMA and the PMAA obtained after exposure and PEB. *Tert*-butyl ester group cleavage is clearly evident from (*i*) the reduction in peak intensity at 3000 cm^{-1} (CH_3 stretch) and 1365 cm^{-1} ($C(CH_3)_3$ stretch), (*ii*) the appearance of a strongly hydrogen bonded broad OH peak at 3100–3400 cm^{-1}, and (*iii*) a peak shift from 1725 cm^{-1} (COOR stretch in PtBMA) to 1700 cm^{-1} (dimeric COOH stretch in PMAA). A reduction of the water contact angle from 88–90° on unexposed surfaces to 75–78° on surfaces after UV exposure and PEB further

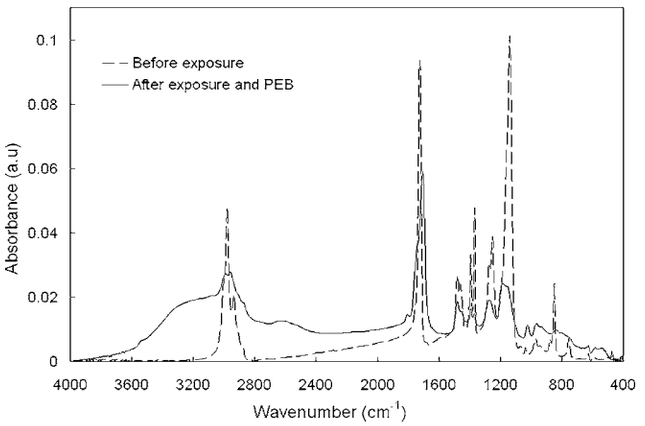

Figure 2. Representative FTIR spectra of the PtBMA polymer used as the reactive imaging film in this work both before exposure and after exposure and PEB.

confirms the generation of hydrophilic OH groups on the surface of the polymer film. These surface hydroxyl groups eventually act as active sites for nucleation of TiO_2 during subsequent ALD processing.

Deposition of TiO_2 was conducted in an ALD reactor that has been described previously.[14] Titanium isopropoxide (TiIP), volatilized at 82°C, was used as the metal precursor, and deionized water maintained at room temperature (~22 to 24°C) was used as the oxygen source for titania deposition by ALD. The reactor was evacuated before starting ALD film deposition to a base pressure of 10–20 mTorr after loading the samples and heating the reactor walls to 90–95°C. Nitrogen was used as both the purge gas and carrier gas, and thus a constant nitrogen flow rate of 78 sccm was maintained throughout the ALD deposition process. All depositions were conducted at a chamber pressure of 1 Torr and a substrate temperature of 140°C. The ALD precursor pulse and purge sequence times for all the depositions was fixed at 2 s (TiIP)-25 s (N_2)-2 s (H_2O)-60 s (N_2). Under these operating conditions TiO_2 has been measured to grow at a controlled growth rate of approximately 0.07 nm per cycle. During ALD, the absence of hydroxyl sites on the unexposed regions of the polymer film prevents TiO_2 from nucleating in these areas. Active OH sites generated in exposed regions lead to nucleation and growth of a thin, conformal titania film on the polymer surface as demonstrated in the X-ray photoelectron spectra (XPS) presented in Fig. 3. Selective deposition of TiO_2 only in exposed regions is clearly evident from the difference in intensity of the Ti 2p peaks in spectra from the two different regions of a patternwise exposed polymer film. The C 1s peak observed for the titania regions deposited in exposed areas of the polymer film arises from adventitious carbon and not from carbonaceous material incorporation from the polymer film, and thus appears as a single sharp peak at 284.8 eV (C-C bonds). This is clearly distinct from the more complicated C 1s spectra for the polymer as visible in the spectra from the unexposed regions of the sample. These XPS results also indicate the presence of a TiO_2 layer on top of exposed regions of the polymer that has a thickness greater than the attenuation length (~10 nm in this case) of the photoelectrons ejected from the underlying polymer layer. The scanning electron microscopy (SEM) image presented in Fig. 4 also shows that a conformal layer (~21 nm) of TiO_2 is deposited onto the exposed regions of the PtBMA polymer film. Attempts were made to obtain a similar image for the acrylate polymer and the edge transition between the unexposed and exposed regions of a patterned sample. However, the acrylate polymer backbone decomposes under electron beam irradiation in the SEM and thus causes focus problems, which have prevented successful generation of clear images of these other regions at this time. Further work is in progress to more carefully characterize these feature edge transitions and to study high-resolution sub-100 nm features produced using such methods.

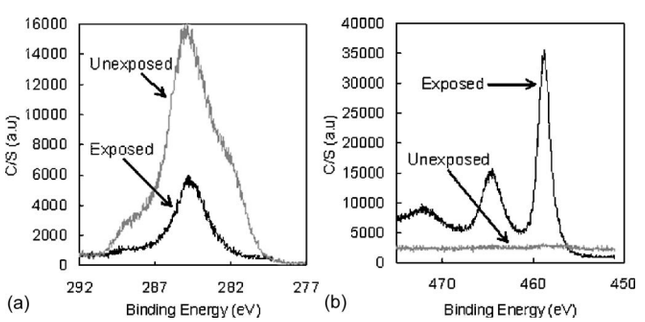

Figure 3. XPS spectra comparing the surface composition of the unexposed and exposed regions of the PtBMA polymer after exposure, PEB, and ALD. (a) C 1s spectra and (b) Ti 2P spectra.

After exposure, baking, and ALD, the inorganic etch barrier pattern is transferred into the polymer layer using an oxygen plasma to obtain a final negative tone image in the polymer film. Plasma pattern transfer etching was performed in a parallel plate plasma reactor operating at 13.56 MHz and 1 Torr O_2. Figure 5 shows optical micrographs of the resulting patterns produced after etch pattern transfer for feature printed using contact lithography at sizes ranging from 25 to 100 μm. While these features are not extremely small, they do demonstrate that the overall process scheme described in Fig. 1 can be successfully applied to allow TSI using an ALD approach. Furthermore, these patterns were produced without the use of a plasma descum etch, furthering lending support to the idea that the metal oxide deposition is highly selective to only the exposed area. Optical and SEM inspection of the samples after imaging, ALD, and etching have not revealed any significant "grass" formation or other residual etch artifacts that have been common in other TSI approaches.

Conclusions

Area selective ALD in conjunction with protected polymer thin films offers a promising approach to achieve high-resolution top

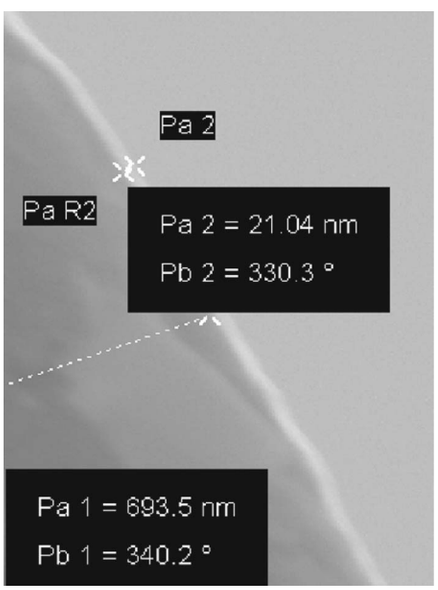

Figure 4. Cross-sectional SEM image showing conformal TiO_2 layer grown on PtBMA film after UV exposure and PEB.

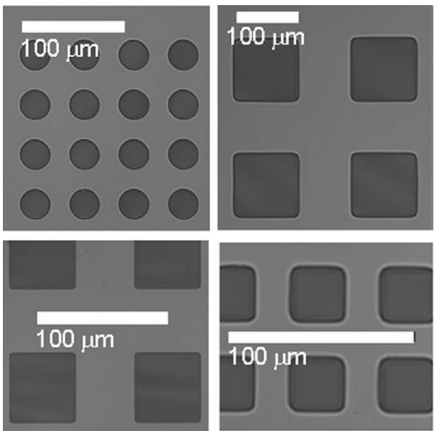

Figure 5. Optical micrographs showing different size and shape patterns obtained after completion of the four-step process illustrated in Fig. 1. ALD precursors: titanium isopropoxide and water, photoresist: PtBMA formulated with a PAG.

surface imaging. Direct area selective patterned growth of titania on a chemically amplified protected polymer film and subsequent pattern transfer by oxygen plasma etching has been demonstrated. It has been shown that successful pattern transfer can be achieved without requiring a plasma descum etch, thus simplifying the TSI process. Further characterization of the capabilities and behavior of such processes is in progress and will be reported in the near future. Optimization of the overall scheme and investigations to assess LER are currently underway.

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References

1. R. Dammel, *Diazonaphthoquinone-based Resists*, Vol. TT 11, SPIE-The International Society for Optical Engineering, Bellingham, WA (1993).
2. C. G. Willson, L. F. Thompson, and M. J. Bowden, *Introduction to Microlithography*, 2nd ed., American Chemical Society, Washington, DC (1994).
3. D. E. Seeger, D. C. La Tulipe, Jr., R. R. Kunz, C. M. Garza, and M. A. Hanratty, *IBM J. Res. Dev.*, **41**, 105 (1997).
4. M. H. Somervell, D. S. Fryer, B. Osborn, K. Patterson, J. Byers, and C. G. Willson, *J. Vac. Sci. Technol. B*, **18**, 2551 (2000).
5. F. Coopmans and B. Roland, *Solid State Technol.*, **30**, 93 (1987).
6. C. M. J. Mutsaers, F. A. Vollenbroek, W. P. M. Nijssen, and R. J. Visser, *Microelectron. Eng.*, **11**, 497 (1990).
7. C. Pierrat, S. Tedesco, F. Vinet, M. Lerme, and B. Dal'Zotto, *J. Vac. Sci. Technol. B*, **7**, 1782 (1989).
8. C. G. Willson, and M. J. Bowden, *Adv. Chem. Ser.*, **218**, 75 (1988).
9. International Technology Roadmap for Semiconductors, 2004 Update.
10. T. Sugihara, F. Van Roey, A. M. Goethals, K. Ronse, and L. Van Den Hove, *Microelectron. Eng.*, **46**, 339 (1999).
11. S. Mori, T. Morisawa, N. Matsuzawa, Y. Kaimoto, M. Endo, T. Matsuo, K. Kuhara, and M. Sasago, *J. Vac. Sci. Technol. B*, **16**, 3739 (1998).
12. M. H. Park, Y. J. Jang, H. M. Sung-Suh, and M. M. Sung, *Langmuir*, **20**, 2257 (2004).
13. M. Yan, Y. Koide, J. R. Babcock, P. R. Markworth, J. A. Belot, T. J. Marks, and R. P. H. Chang, *Appl. Phys. Lett.*, **79**, 1709 (2001).
14. A. Sinha, D. W. Hess, and C. L. Henderson, *J. Electrochem. Soc.*, **153**, G465 (2006).
15. A. Sinha, D. W. Hess, and C. L. Henderson, Journal of Vacuum Science & Technology, B: Microelectronics and Nanometer Structures, Submitted.
16. H. Ito and M. Ueda, *Macromolecules*, **21**, 1475 (1988).